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Transfer hydrogenation with abnormal dicarbene rhodium(III) complexes containing ancillary and modular poly-pyridine ligands†

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Treatment of an abnormal dicarbene ligated rhodium(III) dimer with 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) or 2,2':6',2''-terpyridine (terpy) results in coordination of the *N*-donor ligands and concomitant cleavage of the dimeric structure. Depending on the denticity of the pyridyl ligand, this situation retains one (L = terpy) or two (L = bipy, phen) flexible sites for substrate coordination. In the case of the bipy complexes, modification of the electron density at Rh, without directly affecting the steric environment about the metal centre, was achieved by the incorporation of electron-donating or electron-withdrawing substituents on the bipy backbone. The dicarbene pyridyl complexes were active in transfer hydrogenation catalysis of benzophenone at 0.15 mol% catalyst loading in a iPrOH/KOH mixture. The catalysts displayed a strong characteristic colour change (yellow to purple) after activation which allowed for visual monitoring of the status of the reaction. The colour probe and the robustness of the active catalysts proved useful for catalyst recycling. The catalytic activity sustained over five consecutive substrate batch additions and gave a maximum overall turnover number of 3100.

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Introduction

Poly-pyridines and in particular 2,2'-bipyridine (bipy) and 2,2',6',2''-terpyridine (terpy) have been extensively explored as ligands for transition metals, metalloids and main group elements due to the attractive features they impart onto the coordinated centre.¹ As ligands, they have numerous applications in catalysis,² such as C–H borylations,³ alcohol⁴ and/or water oxidation,⁵ the aldehyde–water shift reaction,⁶ and simple hydrogenation chemistry.⁷ The pyridyl groups can be electronically modified by incorporation of electron-donating (EDGs) or electron-withdrawing substituents (EWGs) at, for example, the 4,4'-position of bipy. Such substitution offers an approach to tune the properties of the metal centre and thus a flexible handle on catalyst optimisation. With the ongoing development of poly-pyridines and their relatives as privileged ligands

for homogeneous catalysis, and with the emergence of *N*-heterocyclic carbenes (NHCs) as a versatile class of strong σ -donating ligands for transition metals,⁸ a combination of the two scaffolds is a logical field for investigation. For example, the replacement of one or more of the pyridine units with an NHC fragment,⁹ such as in bipy¹⁰ and terpy¹¹ ligand systems, has been investigated. Another strategy involves fusing an NHC onto a pyridyl group such as that of a phenanthroline¹² or bipyridine¹³ unit, which gives *inter alia* the CNN analogue of a catalytically very active PNN pincer-type ligand. Complexes incorporating these ligands, specifically complexes of Ru, are active catalysts for the hydrogenation of amides to alcohols.¹⁴ Much work in ruthenium polypyridine and NHC chemistry has surely been spurred by the advances made in both materials development and photochemistry. This latter aspect is a result of the fact that pyridyl-bound metal centres are, in particular, very useful for the conversion of light to energy and for the fabrication of supramolecular assemblies.¹⁵ Some recent reviews have covered the use of NHC ligands in transition metal complexes as components for materials science applications.¹⁶ While fused pyridyl-NHC metal complexes have attracted much interest,^{10,11,17} pyridyl and NHC ligands bound independent of each other to the metal centre have been less investigated.¹⁸ Based on the established impact of poly-pyridine ligands, we were interested in exploring pyridyl donors as ligands in conjunction with a chelating

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C4-diimidazolyldiene rhodium(III) scaffold for transfer hydrogenation catalysis.¹⁹ Such abnormal or mesoionic ligands²⁰ are strongly donating and have shown to enhance the catalytic activity of the metal center in several cases.²¹ In the set-up designed here, the chelating dicarbene and bipyridyl ligands bound to Rh leave two flexible sites available for possible hydride ligation and substrate interaction. On the other hand, terpy typically binds in a meridional $\kappa^3\text{-N,N',N''}$ coordination mode, which would leave only a single site available for substrate interaction, likely situated *trans* to one carbene bonding site. The strong *trans* effect of the carbene offers potential to enhance activity, such as by accelerating the product dissociation step in the catalytic cycle. Thus, we aimed at exploring bipy and terpy as ligands to furnish an active Rh(dicarbene) scaffold for transfer hydrogenation catalysis.

Results and discussion

Synthesis of dicarbene pyridyl complexes

Compound **1**, a mono-cationic formal $[\text{Rh}^{3+}]_2$ dimeric complex, was synthesised as previously described in the literature.²² Coordination of bipy, phen or terpy resulted in cleavage of the dimeric structure of **1** to give the bench-stable mono-metallic species **2**, **3**, and **4**, respectively (Scheme 1).

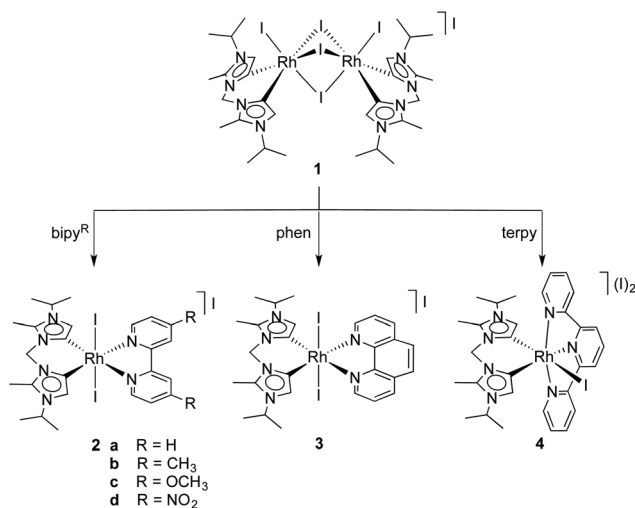
The ^1H NMR spectroscopic data indicated only one set of bipy signals for **2** which suggests a C_{2v} -symmetric complex in solution, in which the bipy *N*-atoms are in *trans* position to the carbene carbons. The ^1H NMR signals of the bipy display characteristic downfield shifts due to the reduced electron density about bipy when donating electron density to the Rh centre. For example, the protons *ortho* to the bipy nitrogens shift from $\delta_{\text{H}} = 8.66$ (free bipy) to 9.35 ppm in **2a** (both in CD_2Cl_2). The NCH_2N bridge and the *i*Pr methyl groups of the carbene ligand in complexes **2a–d** appear as broad signals at room temperature (RT) indicating slow inversion of the boat-

like metallacycle on the NMR timescale. The signals were well resolved on cooling the sample to -20°C and completely coalesce to a broad singlet upon heating to about 60°C (CD_3CN). From the coalescence temperature (T_c), the free energy of inversion (ΔG^\ddagger) for the dicarbene metallacycle was estimated at 63 ± 1 kJ mol $^{-1}$ for **2a** and identical within experimental error at 62 ± 1 , 61 ± 1 and 61 ± 1 kJ mol $^{-1}$ for **2b–d**, respectively. Calculating the free energy of inversion based on the T_c of the *i*Pr methyl groups gave values within the standard deviation and are thus identical to the ΔG^\ddagger calculations based on the coalescence of the NCH_2N resonances. The substituent on the bipy backbone has a direct effect on the chemical shift of the bipy protons. The *ortho* bipy protons of **2c** ($\delta_{\text{H}} = 9.12$), with the electron-donating methoxy group, are more shielded than for **2a** ($\delta_{\text{H}} = 9.38$) while those of **2d**, with electron-withdrawing $-\text{NO}_2$ substituents are significantly more deshielded ($\delta_{\text{H}} = 9.70$; CD_3CN).

Tuning of the electron density about Rh, by incorporating electron-donating or electron-withdrawing groups at the *para* position of the pyridine ring was suggested by NMR spectroscopic analyses of the $\text{C}_{\text{imid}}\text{--H}$ proton resonances (Table 1). Albeit weak, the observed shift differences are diagnostic. Thus when compared to **2a** ($\delta_{\text{H}} = 7.29$), this signal shifts upfield when an electron-donating substituent is incorporated (methyl; methoxy: $\delta_{\text{H}} = 7.26$; 7.23), and it is more deshielded in **2d** featuring an electron-withdrawing nitro group ($\delta_{\text{H}} = 7.32$). Similarly, the ^{13}C NMR signals for the metal-bound carbenic nucleus $\text{C}_{\text{imid}}\text{--Rh}$ were slightly more deshielded in **2b** and **2c** ($\delta_{\text{C}} = 137.6$, $\text{R} = \text{Me}$, and 137.9, $\text{R} = \text{OMe}$, respectively) when compared to **2a** ($\delta_{\text{C}} = 137.4$). This nucleus is considerably more shielded in **2d** ($\delta_{\text{C}} = 135.3$). These data suggest that the electronics of the Rh centre can be finely modulated without affecting the steric environment about the metal center. Interestingly, though, the Rh–C coupling constants were not sensitive to the modulated donor properties of the *trans*-positioned bipy. Much like the activation energy for metallacycle inversion (see above), no clear trend was apparent in complexes **2a–d** for the Rh–C coupling constants ($J_{\text{CRh}} = 36.9 \pm 0.4$ Hz).

The phen complex **3** showed generally more deshielded ^1H NMR resonances compared to those of **2a**, including a lower field signal for the $\text{C}_{\text{imid}}\text{--H}$ protons ($\delta_{\text{H}} = 7.42$). The NCH_2N and *i*Pr methyl proton signals also appeared as broad multiplets at RT indicating slow inversion of the dicarbene metallacycle.

For the terpyridine complex **4**, desymmetrisation of the complex was apparent by the two inequivalent sets of ^1H and ^{13}C NMR signals for the dicarbene ligand. For example, the



Scheme 1 Synthesis of dicarbene rhodium(III) complexes **2–4** bearing bipy, phen or terpy ligands.

Table 1 ^1H and ^{13}C NMR data and free energy of dicarbene metallacycle inversion for complexes **2a–d** (in CD_3CN)

Complex	$\text{C}_{\text{imid}}\text{--H}$ (ppm)	C_{imid} (ppm)	J_{CRh} (Hz)	ΔG_{av} (kJ mol $^{-1}$)
2a	7.29	137.4	36.5	63 ± 1
2b	7.26	137.6	36.8	62 ± 1
2c	7.23	137.9	36.8	61 ± 1
2d	7.32	135.3	37.3	61 ± 1



two carbene C-atoms for **4** resonate at $\delta_{\text{C}} = 141.0$ ($^1J_{\text{CRh}} = 38.5$ Hz) and 133.2 ($^1J_{\text{CRh}} = 42.1$ Hz) ppm. Likewise, in the ^1H NMR spectrum, the C-CH₃ signals appeared as two singlets at $\delta_{\text{H}} = 2.91$ and 2.61 each integrating for three protons. The C_{imid} protons were significantly separated ($\delta_{\text{H}} = 7.68, 5.89$). The higher field resonance indicates a significant shielding effect of the terpy π -system on the proximal imidazolylidene proton, while the more distant imidazolylidene proton showed a more typical resonance value. Inversion of the metallacycle is more facile in **4** than in complexes **2a–d** since the methylene linker appears as a singlet resonance at $\delta_{\text{H}} = 6.02$.

X-ray crystallography

Structural data was obtained for complexes **2a**, **2b** and **4** from X-ray diffraction studies (Fig. 1) which unambiguously confirmed that both bipy N-atoms are *trans* to a carbene in complexes **2a/b**. Selected bond lengths and angles are shown in Table 2. For these two compounds, the Rh atom resides in a slightly distorted octahedral geometry comprised of the dicarbene ligand, bipy and two iodido ligands in a mutually *trans* arrangement. The dicarbene rhodacycle adopts a boat-type geometry in the solid state. The average Rh–C bond length of 2.013 Å is within the expected range,²³ and slightly longer than that found in related Rh(III) complexes which bear two acetonitrile ligands instead of a chelating bipy (average Rh–C = 1.985 Å).²² The Rh–N bond lengths for **2b** are slightly longer than those of **2a** perhaps pointing to an electronic effect of the

Table 2 Selected bond lengths (Å) and angles (°) for **2a**, **2b** and **4**

	2a (X = I2)	2b (X = I2)	4 (X = N7)
Rh–C1	2.011(2)	2.024(5)	2.026(5)
Rh–C9	2.006(2)	2.011(2)	2.011(5)
Rh–N5	2.1273(18)	2.145(4)	2.062(5)
Rh–N6	2.1263(17)	2.131(4)	1.998(4)
Rh–I1	2.6543(2)	2.6505(5)	2.7464(5)
Rh–X	2.6810(2)	2.6943(5)	2.066(5)
C1–Rh–C9	84.14(8)	85.31(18)	87.0(2)
C1–Rh–N6	174.95(8)	175.56(18)	177.8(2)

more electron-donating 4,4'-Me₂-bipy ligand. For **4**, the meridionally binding terpy ligand restricts coordination of the iodido ligand to the position *trans* to the carbene. The Rh–I bond length of 2.7464(5) Å is longer than those of **2** (average Rh–I = 2.670 Å), highlighting the strong *trans* influence of the carbene ligand. The Rh–C bond lengths are identical within standard deviations and thus suggest that the iodine and the pyridine N-atoms have a similar *trans* influence.²⁴ Meridional binding of the terpy ligand in **4** allows for an almost ideal dicarbene bite angle to Rh (C–Rh–C 87.0(2)°). However, distortion from octahedral geometry is apparent by the N5–Rh–N7 angle of 159.73(19)°. Of note, the proton bound to C10 is rather close to the central pyridyl ring (H10...Cg_{pyr} 3.30 Å), which is in agreement with a strong shielding of that proton in the ^1H NMR spectrum due to ring current effects.

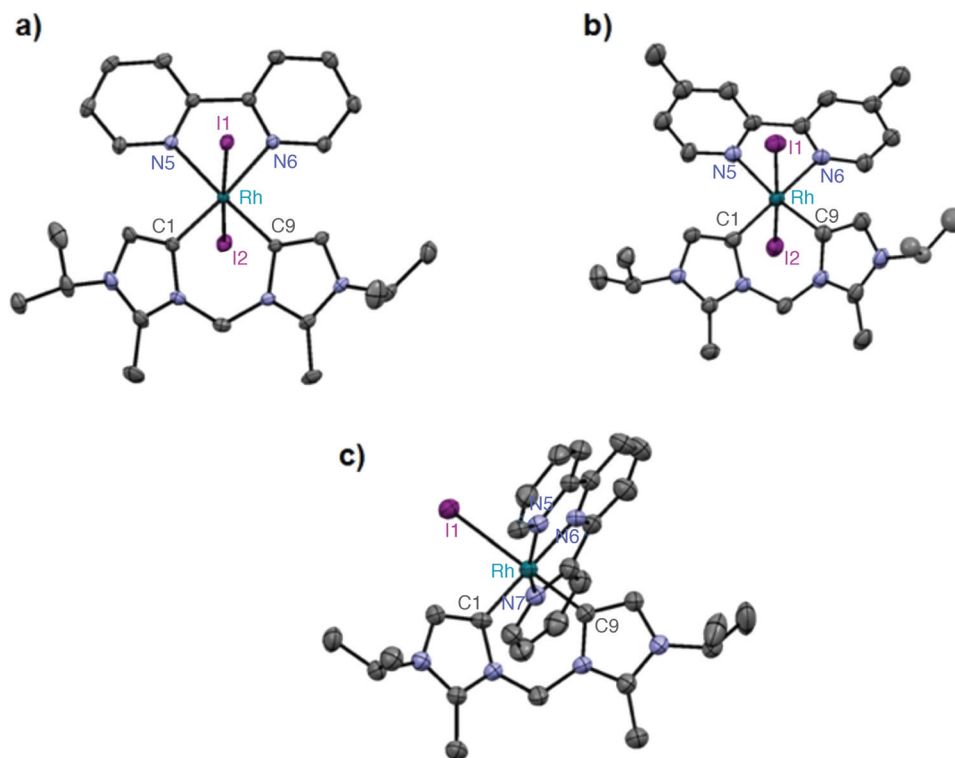


Fig. 1 ORTEP representation of the cationic portions of **2a** (a), **2b** (b) and **4** (c). Ellipsoids are drawn on the 50% probability level. Hydrogen atoms and co-crystallised solvent molecules have been omitted for clarity.



Catalytic transfer hydrogenation

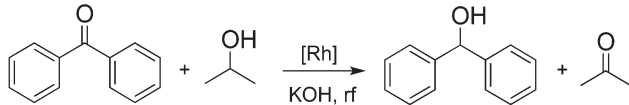
The activity of complexes **2**, **3** and **4** in hydrogen transfer catalysis was evaluated using 2-propanol as the formal H₂ donor and benzophenone as a model acceptor (Table 3).²⁵ Typically, the active catalyst was formed by heating the precursor complex in basic iPrOH to reflux temperature for 10 min before benzophenone was added. At 0.15 mol% catalyst loading, most imine complexes showed enhanced catalytic activity when compared to dimer **1**. The latter gave 50% conversion after 2 h and did not reach full conversion after 24 h (82%, entry 1). Complex **2a** and **2b** were significantly more active and afforded hydrogenated diphenylmethanol in quantitative yields after 2 and 3 h, respectively (entries 2 and 3). Tuning of the catalytic activity was expected by incorporation of electronically active groups on the bipy backbone. Intriguingly, modification of the bipy by incorporating electron-donating or withdrawing groups resulted in poorer conversions than **2a** (which contains a H-atom in the bipy *para* positions). A methyl group at the *para* position of the pyridine ring slowed the catalysis compared to **2a** which is particularly evident at early onset reaction times (entry 3). Much more detrimental was heteroatom substitution at the 4,4'-position of bipy as shown by **2c** and **2d**, which both gave only very poor conversion values (entries 4 and 5). The more rigid diimine system **3** led to a catalyst with similar activity to **2a** (*cf.* entry 6). In contrast, complex **4** containing a terpy ligand was slower than **2a** and showed essentially the same activity as the imine free dimer **1** and full conversion was only reached at prolonged reaction times (entry 7). Presumably the availability of only one site for substrate coordination decelerates catalytic turnovers. It is worth noting that while the diimine ligand does accelerate the transfer hydrogenation catalysis (*cf.* entries 1 and 2), the activity is less enhanced than when incorporating

diphosphine ligands.²⁶ Related rhodium systems containing a dicarbene ligand scaffold are considerably less active.²⁷

Interestingly, formation of the catalytically active species during the substrate-free initiation period was indicated by a distinct colour change of the reaction mixture from yellow to deep purple (complexes **2** and **3**, Fig. 2) or bright green (for **4**). When using the less active complexes **2c** and **2d**, a colour change to reddish/brown was observed after heating to reflux in the presence of KOH (10 min.). After full conversion of benzophenone, the colour of the reaction mixtures remained purple for some time, and changed back to yellow only after extended periods of stirring. The same colour change was observed upon cooling the reaction mixtures at partial conversion. With further heating (to induce full conversion), the purple colour was again established. These observations suggest that the purple colour is associated with a compound that only persists at elevated temperatures and that is related to the catalytically active species. The yellow colour is thus diagnostic of a dormant state of the catalyst derived from **2a**, while the purple species is correlated with catalytic activity. This colour change reveals a useful diagnostic tool to evaluate the status of the catalytic reaction for all the complexes **2–4**. Accordingly, the catalyst remains in its active form even after full consumption of the substrate, but gradually deactivates after full conversion, as indicated by the colour change from purple back to yellow after extended periods of stirring (>10 h) when full conversion was reached. Presumably, evaporation of acetone prohibits a steady state hydrogen transfer equilibrium.

To further investigate the nature of the active species, a series of temperature- and solvent-dependent experiments were performed to identify the source of the colour change. The purple species was only observed in solvents such as iPrOH and cyclohexanol which contain a H-atom α to that of

Table 3 Catalytic transfer hydrogenation of benzophenone with rhodium(III) dicarbene pyridyl complexes^a

						
Entry	[Rh]	Mol% [Rh]	Conversion			TON
			0.5 h	2 h	3 h	
1	1	0.15	26	50	82 ^b	330
2	2a	0.15	26	97	99	660
3	2b	0.15	9	70	97	650
4	2c	0.15	8	34	50	330
5	2d	0.15	17	47	66	440
6	3	0.15	22	97	100	670
7	4	0.15	22	56	93 ^b	620
8	—	—	<2	<2	<2	—

^a General conditions: benzophenone (3 mmol), iPrOH (15 mL), KOH (0.3 mmol), reflux temperature. KOH was added as a 2 M aqueous solution; conversions and yields identical, averages of at least two runs with deviations of max $\pm 3\%$ except entry 5, deviation max 10%.

^b Conversion after 24 h.

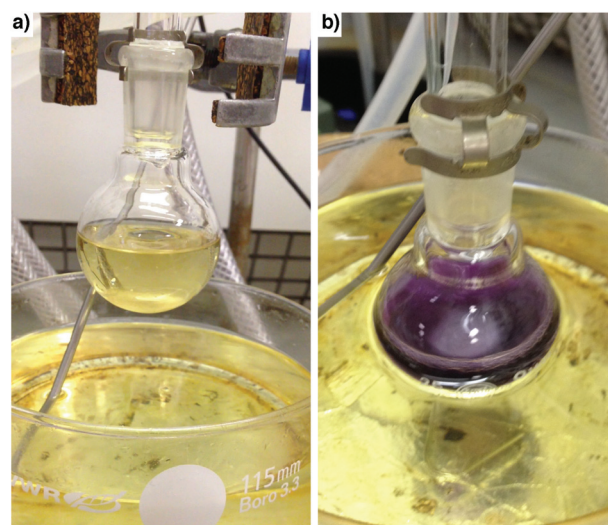
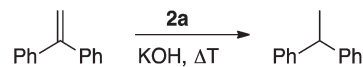


Fig. 2 Colour change of solutions containing the dormant catalytically inactive form derived from complex **2a** (a; yellow solution), and the catalytically active form (b; purple solution).



the alcohol group. When using *t*BuOH, with KOH as base, or in 1,2-dichloroethane at reflux temperature, no colour change of **2a** nor any catalytic hydrogen transfer was observed. Similarly, no colour change was observed when **2a** was refluxed in *i*PrOH without KOH. Therefore, the colour change is probably not associated with the formation of an alkoxide species and may originate instead from a hydride complex that is formed after β -hydride elimination of the alkoxide.²⁸ Indeed, catalytic transfer hydrogenation with **2a** can also be carried out with cyclohexanol as the H₂ source. At 160 °C, 24% conversion of benzophenone to diphenylmethanol was reached after 4 h and the solution mixture was again purple in colour. In a parallel run in cyclohexanol at 110 °C (*i.e.*, the typical temperature used for transfer hydrogenation with *i*PrOH), the mixture remained yellow throughout and was essentially inactive (<5% conversion after 4 h). These temperature dependent studies support the fact that the purple species only forms at vigorous reflux, possibly to advance the β -hydride elimination from the alkoxide by removal of the corresponding ketone.

The colour-activity relationship and the robustness of the active species derived from **2a** were utilised in a recycling experiment. To this end, a reaction was launched with the same substrate/base/catalyst ratio (6 mmol benzophenone, 0.15 mol% **2a**, 30 mL *i*PrOH) and every 2.5 hours, conversions were determined and a fresh batch of benzophenone (6 mmol) was added (Fig. 3). The conversions, were high for each addition of benzophenone (typically >90%) and the reaction mixture remained active and purple in colour over five consecutive additions of substrate. The fifth batch was stirred for 14 rather than just 2.5 h, and while this extended reaction time did not affect yields (overall >92%), the colour of the solution changed back to yellow during this period. Addition of a sixth batch of benzophenone did not lead to significant conversions anymore and the catalytic activity effectively ceased. Thus, an overall yield of 92% (30 mmol benzophenone) and a turnover number (TON) of 3100 over five batches of benzophenone was achieved with **2a**. Similarly high turnovers have been



Scheme 2 Transfer hydrogenation of 1,1-diphenylethylene with **2a**.

obtained with rhodium complexes containing specific carbene spectator ligands.²⁹

Typically, the status of catalytic reactions can rarely be determined visually by simply monitoring the reaction mixture. For example, the imine-free complex **1** or related dicarbene Rh(III) complexes containing diphosphine spectator ligands displayed no colour changes throughout the same transfer hydrogenation catalysis.²⁶ The colour change observed in this work appears to be specific to complexes **2**, **3** and **4** and probably involves in some way the pyridyl ligand, perhaps by a hydride migration process. Chirik and co-workers have observed ligand-centred radicals and migration of hydrides and alkyl groups to the 4-position of a metal-bound pyridine unit in a cobalt complex.³⁰ The lower conversions of the catalysis when incorporating substituents, whether electron-donating or -withdrawing, on the 4,4'-positions of the bipy ligand (**2b–d**) is unexpected and may hint at a similar involvement of the pyridine unit in complexes **2a–d**. Hence, hydride migration from the Rh centre to the bipy may occur and may be more sterically hindered in the case of **2b–c** when compared to that of **2a**. In an attempt to probe such a migration, a catalytic run with the deuterated hydrogen donor (CD₃)₂CDOH as solvent was carried out. Approximately 91% deuterium incorporation was noted at the carbinol carbon of the formed diphenylmethanol, thus indicating a monohydride mechanism for the hydrogen transfer.³¹ The Rh species recovered at the end of the process did not reveal any deuterium incorporation into the aromatic region (²H NMR spectroscopy). In another attempt to determine if migration to the 4-position of bipy was occurring, a standard catalytic run was set up with **2a** and using 1,1-diphenylethylene as substrate which may migrate to the pyridyl ligand.³⁰ While full conversion to the corresponding alkane was observed after 14 h, no migrated pyridyl-bound alkyl species was detected by either NMR spectroscopy or mass spectrometry. Even though these experiments thus do not provide any further mechanistic insights, they demonstrate that complex **2a** is also an efficient catalyst for transfer hydrogenation of hydrocarbon olefins (Scheme 2).³² Hence, bipy coordination is an attractive extension for Rh-catalysed hydrogen transfer catalysis as this ligand enhances the catalytic performance of the metal centre and offers a convenient visual indicator of the catalytic activity.

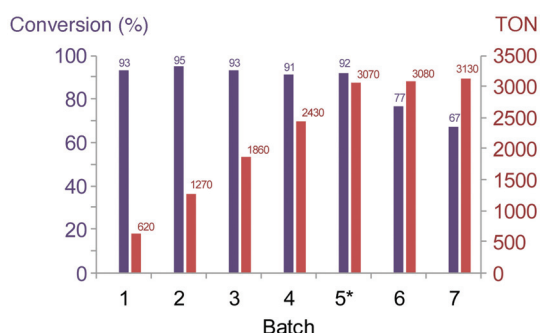


Fig. 3 Repetitive addition of benzophenone for transfer hydrogenation using **2a** showing total conversion (purple, determined 2.5 h after addition of benzophenone) and aggregated turnover number (TON, red). Benzophenone was added every 2.5 h, except for the 6th batch, which was added only after 14 h (*).

Conclusions

A series of air-stable pyridyl coordinated formally Rh(III) dicarbene complexes, bearing bipy, phen or terpy, have been synthesised in high yields and utilised for transfer hydrogenation in *i*PrOH/KOH. Pyridyl ligand incorporation enhances the



activity of the dicarbene rhodium(III) system for this hydrogenation involving benzophenone at low catalyst loadings (0.15 mol%). The active species display a visual signature for determining the status of the reaction based on a vivid colour change (yellow to purple or green) upon activation. Temperature and solvent-dependent studies indicate that the colour change is probably associated with a Rh–H species formed following β -hydride elimination of a coordinated alkoxide at elevated temperatures during the catalytic cycle. The correlation between the colour of the reaction and the catalytically active species is unusual and offers further potential in catalysis investigations. For example, sampling of the catalytic reaction is often disruptive to the reaction rate and may be circumvented using the UV-Vis properties rather than intrusive sampling. The colour of the reaction enables a visual determination of whether the catalytically active species still persists and is thus particularly useful for recycling experiments. Incorporation of aliphatic diamines or diimines to the dicarbene Rh(III) platform, rather than aromatic diimines reported here, may shed further light on the source of the colour change on catalyst activation.

Experimental section

General comments

All syntheses were carried out under ambient conditions unless otherwise stated and all reagents and solvents were used as received from commercial suppliers. The diimidazolium salt and complex **1** were prepared according to literature procedures.²² Unless specified, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 25 °C on Varian spectrometers operating at 300, 400, 500 or 600 MHz (^1H NMR) and 101, 126 or 151 MHz (^{13}C NMR) respectively. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to residual solvent signals (^1H , ^{13}C). Assignments are based on homo- and heteronuclear shift correlation spectroscopy. Elemental analyses were performed at UCD Microanalytic Laboratory using an Exeter Analytical CE-440 elemental analyser. High-resolution mass spectrometry was carried out with a Micromass/Waters Corp. USA liquid chromatography with an electrospray source. RT is 18 °C unless otherwise stated.

General procedure for the synthesis of complexes **2a–d**, **3** and **4**

The dimeric complex **1** was dissolved in CH_2Cl_2 (20 mL) and the relevant pyridyl compound was added (2.2 equiv.: 1.1 equiv. per Rh atom). The solution was stirred for 16 h at RT. The resulting suspension was added to a centrifuge vessel with Et_2O (80 mL) and the precipitate was then isolated by centrifugation and decantation. The orange residue was re-dissolved (CH_2Cl_2 : 10 mL) and precipitated again with Et_2O (80 mL). Following centrifugation and decantation of the supernatant, the recovered residue was dried under reduced pressure to yield the pure product.

[RhI₂(C,C-dicarbene)(2,2'-dipyridyl)]I (2a). Following the general procedure, complex **1** (200 mg, 0.13 mmol) and 2,2'-bipyridine (42 mg, 0.27 mmol) afforded **2a** (190 mg, 78%) as a yellow coloured solid. Crystals of **2a** for X-ray diffraction studies were grown by slow evaporation of an MeCN solution of the complex. ^1H NMR (253 K, 600 MHz, CD_3CN): δ = 9.38 (d, 2H, $^3J_{\text{HH}}$ = 5.3 Hz, $\text{H}_{\text{bipy-6}}$), 8.49 (d, 2H, $^3J_{\text{HH}}$ = 8.1 Hz, $\text{H}_{\text{bipy-3}}$), 8.13 (m, 2H, $\text{H}_{\text{bipy-4}}$), 7.74 (m, 2H, $\text{H}_{\text{bipy-5}}$), 7.29 (s, 2H, H_{imid}), 6.99 (d, 1H, $^2J_{\text{HH}}$ = 13.1 Hz, lowfield AB part of NCH_2N), 6.15 (d, 1H, $^2J_{\text{HH}}$ = 13.1 Hz, highfield AB part of NCH_2N), 4.57 (septet, 2H, $^3J_{\text{HH}}$ = 6.6 Hz, $\text{NCH}(\text{Me})_2$), 2.70 (s, 6H, $\text{C}_{\text{imid-CH}_3}$), 1.62, 1.40 (d, 6H, $^3J_{\text{HH}}$ = 6.6 Hz, $\text{NCH}(\text{CH}_3)_2$). ^{13}C NMR (253 K, 151 MHz, CD_3CN): δ = 156.1 ($\text{C}_{\text{bipy-2}}$), 152.4 ($\text{C}_{\text{bipy-6}}$), 141.8 (NC_{imidN}), 139.2 ($\text{C}_{\text{bipy-4}}$), 137.4 (d, $^1J_{\text{CRh}}$ = 36.5 Hz, $\text{C}_{\text{imid-Rh}}$), 127.11 ($\text{C}_{\text{bipy-5}}$), 124.0 ($\text{C}_{\text{bipy-3}}$), 123.9 ($\text{C}_{\text{imid-H}}$), 61.2 (NCH_2N), 50.5 ($\text{CH}(\text{Me})_2$), 22.2, 22.1 ($\text{CH}(\text{CH}_3)_2$), 10.5 ($\text{C}_{\text{imid-CH}_3}$). ESI-MS (m/z): 772.9813, calcd for $[\text{M} - \text{I}]^+$ 772.9833. Anal. calcd for $\text{C}_{25}\text{H}_{32}\text{I}_3\text{N}_6\text{Rh}$ (900.18)·0.75 CH_2Cl_2 : C, 32.09; H, 3.50; N, 8.72. Found: C, 32.30; H, 3.17; N, 8.38.

[RhI₂(C,C-dicarbene)(4,4'-dimethyl-2,2'-dipyridyl)]I (2b). Following the general procedure **1** (70 mg, 0.047 mmol) and 4,4'-dimethyl-2,2'-bipyridine (18 mg, 0.098 mmol) afforded **2b** (58 mg, 42%) as a yellow coloured solid. No precipitate was observed after the reaction, however addition of Et_2O (70 mL) induced precipitation of the product in the form of an orange coloured solid. Crystals of **2b** for X-ray diffraction studies were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex. ^1H NMR (253 K, 500 MHz, CD_3CN): δ = 9.19 (d, 2H, $^3J_{\text{HH}}$ = 5.6 Hz, $\text{H}_{\text{bipy-6}}$), 8.36 (s, 2H, $\text{H}_{\text{bipy-3}}$), 7.56 (d, 2H, $^3J_{\text{HH}}$ = 5.6 Hz, $\text{H}_{\text{bipy-5}}$), 7.26 (s, 2H, H_{imid}), 6.97 (d, 1H, $^2J_{\text{HH}}$ = 13.1 Hz, lowfield AB part of NCH_2N), 6.15 (d, 1H, $^2J_{\text{HH}}$ = 13.1 Hz, highfield AB part of NCH_2N), 4.57 (septet, 2H, $^3J_{\text{HH}}$ = 6.6 Hz, $\text{NCH}(\text{Me})_2$), 2.70 (s, 6H, $\text{C}_{\text{imid-CH}_3}$), 2.60 (s, 6H, $\text{C}_{\text{bipy-4-CH}_3}$), 1.61, 1.40 (d, 6H, $^3J_{\text{HH}}$ = 6.6 Hz, $\text{NCH}(\text{CH}_3)_2$). ^{13}C NMR (253 K, 126 MHz, CD_3CN): δ = 155.8 ($\text{C}_{\text{bipy-2}}$), 151.6 ($\text{C}_{\text{bipy-6}}$), 151.2 ($\text{C}_{\text{bipy-4}}$), 141.8 (NC_{imidN}), 137.6 (d, $^1J_{\text{CRh}}$ = 36.8 Hz, $\text{C}_{\text{imid-Rh}}$), 127.8 ($\text{C}_{\text{bipy-5}}$), 124.7 ($\text{C}_{\text{bipy-3}}$), 123.9 ($\text{C}_{\text{imid-H}}$), 61.1 (NC_{imidN}), 50.5 ($\text{CH}(\text{Me})_2$), 22.1 ($\text{CH}(\text{CH}_3)_2$), 20.9 ($\text{C}_{\text{bipy-4-CH}_3}$), 10.5 ($\text{C}_{\text{imid-CH}_3}$). ESI-MS (m/z): 801.0116, calcd for $[\text{M} - \text{I}]^+$ 801.0146. Anal. calcd for $\text{C}_{27}\text{H}_{36}\text{I}_3\text{N}_6\text{Rh}$ (928.23)·0.5 CH_2Cl_2 : C, 34.03; H, 3.84; N, 8.66. Found: C, 34.04; H, 3.42; N, 8.59.

[RhI₂(C,C-dicarbene)(4,4'-dimethoxy-2,2'-dipyridyl)]I (2c). Following the general procedure, **1** (50 mg, 0.034 mmol) and 4,4'-dimethoxy-2,2'-bipyridine (15 mg, 0.069 mmol) afforded **2c** (44 mg, 68%) as an orange coloured solid. ^1H NMR (253 K, 500 MHz, CD_3CN): δ = 9.12 (d, 2H, $^3J_{\text{HH}}$ = 6.4 Hz, $\text{H}_{\text{bipy-6}}$), 8.00 (d, 2H, $^4J_{\text{HH}}$ = 2.6 Hz, $\text{H}_{\text{bipy-3}}$), 7.29 (dd, 2H, $^3J_{\text{HH}}$ = 6.4, $^4J_{\text{HH}}$ = 2.6 Hz, $\text{H}_{\text{bipy-5}}$), 7.23 (s, 2H, H_{imid}), 6.96 (d, 1H, $^2J_{\text{HH}}$ = 13.1 Hz, lowfield AB part of NCH_2N), 6.14 (d, 1H, $^2J_{\text{HH}}$ = 13.1 Hz, highfield AB part of NCH_2N), 4.57 (septet, 2H, $^3J_{\text{HH}}$ = 6.6 Hz, $\text{NCH}(\text{Me})_2$), 4.05 (s, 6H, $\text{C}_{\text{bipy-4-OCH}_3}$), 2.69 (s, 6H, $\text{C}_{\text{imid-CH}_3}$), 1.61, 1.40 (d, 6H, $^3J_{\text{HH}}$ = 6.6 Hz, $\text{NCH}(\text{CH}_3)_2$). ^{13}C NMR (253 K, 126 MHz, CD_3CN): δ = 167.8 ($\text{C}_{\text{bipy-4}}$), 157.5 ($\text{C}_{\text{bipy-2}}$), 153.0 ($\text{C}_{\text{bipy-6}}$), 141.7 (NC_{imidN}), 137.9 ($\text{C}_{\text{imid-Rh}}$, $^1J_{\text{CRh}}$ = 36.8 Hz), 123.7 ($\text{C}_{\text{imid-H}}$), 113.0 ($\text{C}_{\text{bipy-5}}$), 110.6 ($\text{C}_{\text{bipy-3}}$), 61.1 (NCH_2N), 57.0 (OCH_3), 50.4 ($\text{CH}(\text{Me})_2$), 22.1 ($\text{CH}(\text{CH}_3)_2$), 10.5



(C_{imid}-CH₃). ESI-MS (*m/z*): 833.0071, calcd for [M - I]⁺ 833.0044. Anal. calcd for C₂₇H₃₆I₃N₆O₂Rh (960.23): C, 33.77; H, 3.78; N, 8.75. Found: C, 33.96; H, 3.61; N, 9.00.

[RhI₂(C,C-dicarbene)(4,4'-dinitro-2,2'-dipyridyl)]I (2d). Following the general synthesis, **1** (50 mg, 0.034 mmol) and 4,4'-dinitro-2,2'-bipyridine (17 mg, 0.069 mmol) afforded **2d** (40 mg, 59%) as a red coloured solid. ¹H NMR (253 K, 500 MHz, CD₃CN): δ = 9.70 (d, 2H, ³J_{HH} = 6.0 Hz, H_{bipy-6}), 9.40 (d, 2H, ³J_{HH} = 2.0 Hz H_{bipy-3}), 8.49 (dd, 2H, ³J_{HH} = 6.0 Hz, ⁴J_{HH} = 2.0 Hz, H_{bipy-5}), 7.32 (s, 2H, H_{imid}), 6.94 (d, 1H, ²J_{HH} = 13.2 Hz, lowfield AB part of NCH₂N), 6.16 (d, 1H, ²J_{HH} = 13.2 Hz, highfield AB part of NCH₂N), 4.59 (septet, 2H, ³J_{HH} = 6.6 Hz, NCH(Me)₂), 2.71 (s, 6H, C_{imid}-CH₃), 1.64, 1.41 (d, 6H, ³J_{HH} = 6.6 Hz, NCH(CH₃)₂). ¹³C NMR (253 K, 126 MHz, CD₃CN): δ = 157.2 (C_{bipy-2}), 155.6 (C_{bipy-4}), 155.2 (C_{bipy-6}), 142.4 (NC_{imid}N), 135.3 (d, ¹J_{CRh} = 37.3 Hz, C_{imid}-Rh), 123.9 (C_{imid}-H), 120.6 (C_{bipy-5}), 118.6 (C_{bipy-3}), 61.4 (NCH₂N), 50.7 (CH(Me)₂), 22.2, 22.1 (CH(CH₃)₂), 10.6 (C_{imid}-CH₃). ESI-MS (*m/z*): 862.9495, calcd for [RhI₂(C,C-dicarbene)(4,4'-dinitro-2,2'-dipyridyl)]⁺ 862.9535. Anal. calcd for C₂₅H₃₀I₃N₈O₄Rh (990.18): C, 30.32; H, 3.05; N, 11.32. Found: C, 30.04; H, 2.94; N, 11.07.

[RhI₂(C,C-dicarbene)(1,10-phen)]I (3). Following the general procedure, complex **1** (53 mg, 35.6 μmol) and 1,10-phenanthroline (14 mg, 78.4 μmol) afforded **3** (62 mg, 86%) as an orange coloured solid.

¹H NMR (500 MHz, CD₃CN): δ = 9.73 (dd, 2H, ³J_{HH} = 5.1 Hz, ⁴J_{HH} = 1.4 Hz, H_{phen}), 8.70 (dd, 2H, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 1.4 Hz, H_{phen}), 8.21 (s, 2H, H_{phen}), 8.09 (dd, 2H, ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 5.1 Hz, H_{phen}), 7.42 (s, 2H, H_{imid}), 7.11, 6.24 (br, 1H, NCH₂N), 4.63 (septet, ³J_{HH} = 6.7 Hz, CH(Me)₂), 2.77 (s, 6H, C_{imid}-CH₃), 1.69, 1.48 (br, 6H, NCH(CH₃)₂). ¹³C NMR (253 K, 151 MHz, CD₃CN): δ = 152.9 (C_{phen}-H), 147.5 (C_{phen}), 142.3 (NC_{imid}N), 138.6 (C_{phen}-H), 137.6 (d, ¹J_{CRh} = 37.2 Hz, C_{imid}-Rh), 131.6 (C_{phen}), 128.4 (C_{phen}-H), 126.4 (C_{phen}-H), 124.4 (C_{imid}-H), 61.9 (NCH₂N), 51.2 (NCH(Me)₂), 22.6 (NCH(CH₃)₂), 11.0 (C_{imid}-CH₃). ESI-MS (*m/z*): 796.9936, calcd for [M - I]⁺ 796.9959. Anal. calcd for C₂₇H₃₂I₃N₆Rh (924.20): C, 35.09; H, 3.49; N, 9.09. Found: C, 34.60; H, 3.19; N, 8.79.

[RhI(C,C-dicarbene)(2,2';6',2''-terpyridyl)]I₂ (4). Following the general procedure, **1** (150 mg, 0.10 mmol) and 2,2';6',2''-terpyridine (60 mg, 0.26 mmol) reacted to give **4** (175 mg, 89%) as a bright yellow coloured solid. Crystals of **4** suitable for X-ray diffraction studies were obtained by slow diffusion of Et₂O into a CH₂Cl₂ solution of the complex.

¹H NMR (400 MHz, (CD₃)₂SO): δ = 8.90 (d, 2H, ³J_{HH} = 8.1 Hz, H_{terpy}), 8.78 (d, 2H, ³J_{HH} = 7.9 Hz, H_{terpy}), 8.66 (t, 1H, ³J_{HH} = 8.1 Hz, H_{terpy}), 8.43 (d, 2H, ³J_{HH} = 5.7 Hz, H_{terpy}), 8.28 (td, 2H, ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 1.2 Hz, H_{terpy}), 7.68 (s, 1H, H_{imid}), 7.64–7.59 (m, 2H, H_{terpy}), 6.02 (s, 2H, NCH₂N), 5.89 (s, 1H, H_{imid}), 4.83 (septet, 1H, ³J_{HH} = 6.7 Hz, NCH(Me)₂), 4.34 (septet, 1H, ³J_{HH} = 6.6 Hz, NCH(Me)₂), 2.91 (s, 3H, C_{imid}-CH₃), 2.61 (s, 3H, C_{imid}-CH₃), 1.60, 1.01 (d, 6H, ³J_{HH} = 6.6 Hz, NCH(CH₃)₂). ¹³C NMR (101 MHz, (CD₃)₂SO): δ = 157.4 (C C_{terpy}), 154.5 (C_{terpy}-H), 152.7 (C_{terpy}), 143.33 (NC_{imid}N), 143.27 (NC_{imid}N), 141.2 (C-Rh, ¹J_{CRh} = 38.5 Hz), 140.3 (C_{terpy}-H), 139.9 (C_{terpy}-H), 133.2 (C-Rh, ¹J_{CRh} = 42.1 Hz), 128.1 (C_{terpy}-H), 125.9 (C_{terpy}-H),

125.2 (C_{imid}-H), 124.7 (C_{terpy}-H), 114.2 (C_{imid}-H), 57.7 (NCH₂N), 49.6, 49.5 (CH(Me)₂), 22.3, 21.5 (CH(CH₃)₂), 10.5, 10.2 (C_{imid}-CH₃). ESI-MS (*m/z*): 361.5526, calcd for [M - 2I]²⁺ 361.5527. Anal. calcd for C₃₀H₃₅I₃N₇Rh (977.26)·1CH₂Cl₂: C, 35.05; H, 3.51; N, 9.23. Found: C, 34.77; H, 3.45; N, 9.20.

Typical procedure for catalytic transfer hydrogenation

The precatalyst (4.5 μmol, 0.15 mol%) was weighed directly into the reaction vessel. To the vessel, iPrOH (15 mL) and KOH (0.15 mL of 2 M solution in H₂O: 0.3 mmol) were added and the mixture was then heated to reflux temperature for 10 min. in an oil bath (110 °C). Subsequently, the substrate (3 mmol) was added directly and the reaction was sampled at set time intervals. The samples (0.2 mL) were quenched with cyclohexane (2 mL) and filtered through a short pad of Celite, which was then washed with Et₂O (3 × 2 mL). The combined organic phases were evaporated to dryness (40 °C, 100 mbar) and then analysed by ¹H NMR spectroscopy. Selected runs with hexamethylbenzene as internal standard revealed that spectroscopic conversion of benzophenone and yield of diphenylmethanol were identical under these conditions.

Crystal structure determinations

Crystal data for **2a**, **2b** and **4** were collected using a Rigaku (former Agilent Technologies) Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector and using monochromated Mo-K_α radiation (0.71073 Å) (**2a**) or Cu-K_α (1.54184 Å) (**2b**, **4**). A complete dataset was collected, assuming that the Friedel pairs are not equivalent. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares fitting on *F*² for all data using SHELXL-97.³³ Hydrogen atoms were added at calculated positions and refined by using a riding model. Anisotropic thermal displacement parameters were used for all nonhydrogen atoms except for the disordered isopropyl group in **2b**. The solvents in **4** could not be modelled in terms of atomic size and the SQUEEZE option as incorporated in PLATON was used to compensate for the spread electron density.³⁴ Crystallographic details are compiled in Tables S3 and S4.† Crystallographic data (excluding structure factors) for all three complexes have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1437163 (**2a**), 1437165 (**2b**), and 1437164 (**4**).

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